TARNOSKI

Methyl Mesoxalate and Some of its Reactions

Chemistry

B. S.

1907

UNIVERSITY OF ILL. LIBRARY

UNIVERSITY OF ILLINOIS
LIBRARY

Class 1907 Book T176 Volume

Je 07-10M

Digitized by the Internet Archive
in 2013

http://archive.org/details/methymesoxalates00tarn

METHYL MESOXALATE

AND

SOME OF ITS REACTIONS

BY

PAUL THADDEUS TARNOSKI

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

PRESENTED JUNE, 1907

1907
T176

UNIVERSITY OF ILLINOIS

May 31 1907.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Paul Thaddeus Tarnoski

ENTITLED Methyl Mesoxalate and Some of its Reactions.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Chemistry.

Instructor in Charge.

APPROVED:

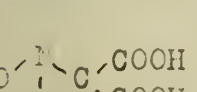
HEAD OF DEPARTMENT OF Chemistry.

102063

The Rare Book & Manuscript Library
URJC

METHYL MESOXALATE AND SOME OF ITS REACTIONS.

Bouveault and Wahl[1] prepared methyl mesoxalate by the reaction of nitrogen peroxide on methyl isonitrosomalonate at a low temperature. Their yield of methyl mesoxalate was poor, being between 35-40%, most of their product being probably saponified by the action of the nitrogen peroxide, and water formed in the reaction.

Willstätter and Hottenroth[2] prepared methyl mesoxalate by heating methyl bromnitromalonate in a distilling flask. The distillate consisted of anhydrous methyl mesoxalate. By adding water, it became a mass of crystals of methyl dihydroxymalonate. Curtiss[3] obtained a 90-95% yield of ethyl mesoxalate by the reaction of nitrous anhydride upon ethyl malonate, and the product was practically pure. Traube[4] formed what he called oxazomalonic acid,  by treating malonic ester with nitric oxide in the presence of sodium ethylate. The product of the reaction which precipitated as an ester, could not be obtained pure, so it was

1) Bull. Soc. Ch. de Paris. (3) Vol. 29. P. 263.
2) Ber. d. Deutsch. Chem. Ges. Vol. 37. P. 1781.
3) Am. Chem. Jour. Vol. 35. P. 477-486.
4) Ber. d. Deutsch. Chem. Ges. Vol. 28. P. 1795.

converted into the sodium salt with alkali.

In the different reactions with the oxides of nitrogen and malonic esters, many different products have been obtained. Conrad and Bischoff[1] made ethyl isonitrosomalonate by treating the sodium salt of ethyl malonate in alcohol solution with the red oxides of nitrogen. Bouveault and Wahl[2] made methyl isonitrosomalonate by passing a current of methyl nitrite through a methyl alcohol solution of the sodium salt of methyl malonate. P. T. Müller[3] made the same product by the saponification of a methyl alcohol solution of nitrosocyanacetic ester with dry hydrochloric acid gas.

In consideration of the low yields and expensive methods thus far devised for making methyl mesoxalate, it was of interest to see if the method already discovered[4] for making the ethyl ester might not be applicable to the lower homologue. The results have shown this to be the case. A yield of 78% of methyl

1) Ann. Chem. (Liebig's) Vol. 209, P. 211.
2) Bull. Soc. Ch. de Paris. Vol. 29, P. 961.
3) Ann. de Ch. et de Ph. Vol. 1. series 7, P. 535.
4) Am. Chem. Journal. Vol. 35, P. 477-486.

mesoxalate has been obtained, and other facts of interest noted.

As we studied particularly the reaction of hydrazine hydrate, and carbonate, upon methyl dihydroxymalonate, a brief resumé of the work done with hydrazine on bodies of this class is given.

In his work on hydrazine, Curtius[1] studied the reaction of hydrazine hydrate on mono and ortho di-ketones. His results show that hydrazine hydrate acts upon ketones in neutral solutions with the formation of bodies having one of two structures: a) and b).

a) $R_2=C=N-N=C=R_2$, when the ketone is added to an excess of hydrazine hydrate. These bodies are very unstable, forming the symmetrical substituted hydrazines, and splitting off hydrazine by the action of cold water.

$$2\ R_2=C=N-N=H_2 + H_2O = R_2=C=N-N=C=R_2 + N_2H_4.H_2O$$

Only a few of these unsymmetrical hydrazines were prepared,

1) Jour. fur Pr. Chemie. Vol. 44, P. 161-166.

great care was necessary to prevent the action of water by having barium oxide present. Phenylmethylmethylenehydrazine[1] was prepared. $C_6H_5 \diagdown C=N-NH_2$ $CH_3 \diagup$ This compound is a liquid which is very sensitive to damp air, the substance changing very easily into the symmetrical bismethylphenylazimethylene according to the reaction: $2\ C_6H_5 \diagdown C=N-NH_2 + H_2O = C_6H_5 \diagdown C=N-N=C \diagup C_6H_5$ $CH_3 \diagup$ $CH_3 \diagup$ $+ N_2H_4H_2O$ Other derivatives of class a) were prepared as above from acetone, and benzophenone, and all show the same characteristic tendency to pass over into the symmetrical azimethylene compounds in the presence of moisture.

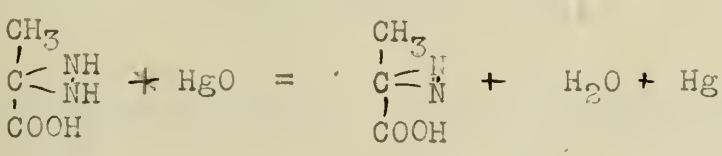
b) $R_2C=N-N=C=R_2$ is formed when two molecules of the ketone are treated with one molecule of hydrazine hydrate. The reaction is easily accomplished with the lower members of the series, as acetone, and methyl ethyl ketone. The greater the number of carbon atoms in the molecule, the more difficult is the reaction; ketones of the phenyl series must be heated in sealed tubes in order to react. This is true of benzo- and acetophenone. The bodies formed are derivatives of azimethylene: $H_2C=N-N=CH_2$.

1) Jour. fur. Pr. Chemie. Vol. 44, P. 540.

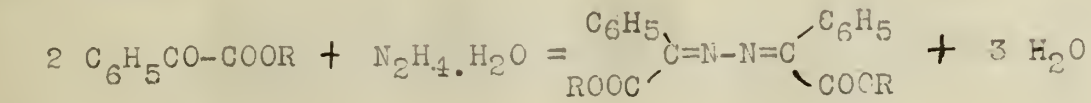
The azimethylene derivatives are not stable toward mineral acids. They split off hydrazine and revert to the original ketones. They are not decomposed by distillation nor by the action of alkalis or alkaline reducing agents.

Curtius and Lang[1] studied the reaction of hydrazine hydrate on alpha ketone acids and esters. Upon alpha oxo propionic acid the reaction goes as follows:

Treated with mercuric oxide, hydrazipropionic acid is converted into alpha diazopropionic acid:



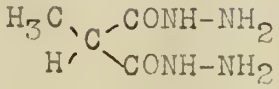
Benzoyl formic ester, when treated with one molecule of hydrazine hydrate, gave the ester of bisphenylazimethylenedi carboxylic acid.[2]



1)Jour. fur Pr. Ch. Vol. 44 P. 554.

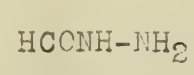
2) Ibid. Page 567.

Carl Bulow[1] studied the reaction of hydrazine hydrate on derivtives of malonic ester, obtaining the hydrazid of mono methyl malonic acid.



Schofer and Schwan[2] studied the reaction of hydrazine hydrate on mono and di-basic acids, and found that hydrazids were formed. The following were prepared:

Malonyl hydrazid.



Formyl hydrazid.

Acetyl Hydrazid.

EXPERIMENTAL.

ACTION OF NITROUS ANHYDRIDE ON METHYL MALONATE:- 25 grams of methyl malonate were placed in a 100 cc. distilling flask. The so called nitrous anhydride was generated by the action of nitric acid, (sp. gr. 1.42) on arsenious oxide. The gas was dried by passing it through a litre flask to condense moisture, and then through a tube two feet long which contained phosphorus pentoxide. A rapid stream of the gas was passed into the ester cooled in a freezing mixture. It dissolved rapidly, and the

1) Ber. d. Deut. Ch. Ges. Vol. 39, P. 3372-77.
2) Jour. fur Pr. Ch. (2) Vol. 51, P. 183.

liquid assumed a light green hue, which became darker and almost opaque at the end of the operation. In one hour and fifteen minutes 25 grams of the ester had absorbed 36 grams of gas, and the volume of the liquid had nearly doubled. The flask and contents were then packed in ice and kept at 0° for about 24 hours. It slowly loses gas all this time, 3-1/2 grams being lost in 45 hours. At this time the weight of the crude green oil was 57.5 grams. The remaining gas was removed by passing a fine stream of air through the liquid at reduced pressure. When most of the gas had passed off, the methyl dihydroxymalonate could be crystallized out and filtered off. 18.5 grams of these crude crystals were thus obtained.

The green mother liquor from these crystals was subjected to fractional distillation in order to obtain the ketone ester, and other products of the reaction.

The distillate was usually separated into three or four fractions. As the pressure was reduced and heat applied, the liquid turned from a green to a dark reddish brown color, and

the apparatus was filled with the red oxides of nitrogen. When the oil was freed from gas it became a pale yellowish green color. The distillation was usually accompanied by two periods of decomposition, the first of which occurred when the distillate was coming at about 70-75° at a pressure of 20-30 mm. The evolution of red gases caused the pressure to increase. The second period occurred toward the last of the distillation process when the temperature had arisen to 130-140° at 20-30 mm. After each decomposition the liquid became a pale green and remained so while the distillation was going on.

The first fraction which was collected from 40-70° at a pressure of 20-40 mm., consisted chiefly of water, a little alcohol, acetic acid, and acetic ester. It had a peculiarly pungent odor, and gave off a gas continually. The remaining product, distilling from 105-125° at 20-30 mm., consisted of 19.0 grams of a thick green oil, and was worked up for methyl dihydroxymalonate.

This oil was treated with 75% of the theoretical amount of water necessary to convert it into the dihydroxy ester. The

temperature rose 40° upon the addition of the water, and a strong, pungent smell was noted. After cooling for a time in ice water, 7.2 grams of crystals were filtered off. The total amount of crystals from 25 grams of methly malonate was 19.7 grams, or a 78% yield. The mother liquor (A) weighed 10.1 grams. This product has been studied and will be described later in this paper.

The crude methyl dihydroxymalonate was recrystallized from dry ether, and showed a melting point of 78°. On slow crystallization from ether, the crystals form in beautiful large monoclinic plates. Methyl dihydroxymalonate is very soluble in water with a decided lowering of temperature. It dissolves easily in acetone, alcohol, and hot benzene. It is fairly soluble in ether and acetic ether, and dissolves with difficulty in cold benzene, chloroform and carbon tetrachloride. It is insoluble in carbon bisulphide and ligroin. The crystals will reduce a warm ammoniacal solution of silver nitrate very quickly, the effect is slower cold.

PREPARATION OF PURE METHYL OXOMALONATE:- The ketone ester

can be prepared by distilling the pure methyl dihydroxymalonate at reduced pressure. When heated above its melting point, the elements of water dissociate and pass over. The keto ester then distills as a grass-green oil. The first runnings recombine with the moisture in the adapter and form pure white crystals of methyl dihydroxymalonate. The second fraction consists of the pure ketone ester, boiling at a constant temperature of 100°(uncor.), under a pressure of 20 mm. with practically no decomposition, a slight residue being left at the end of the experiment.

REACTION OF HYDRAZINE CARBONATE UPON METHYL DIHYDROXYMALONATE:- We have studied the action of solutions of hydrazine hydrate, and hydrazine carbonate, on methyl dihydroxymalonate, and have obtained, a white crystalline product. 2.92 grams of methyl dihydroxymalonate were placed in 1.2 ccs. of 60% hydrazine hydrate, kept cool in ice water. The temperature rose slightly, and in about five minutes white crystals were formed, which were filtered, and washed with water, and ether. The yield was not over 60% and the product was slightly colored. A strong tendency of the reaction products to polymerize into a red gum was noted, so

a solution of hydrazine carbonate was substituted with good results, the same product being formed, with a much higher yield and degree of purity. Three grams of finely ground hydrazine sulphate were added to a solution of 6.6 grams of sodium carbonate in 4 ccs. of water. A brisk evolution of carbon dioxide took place, and a clear solution finally resulted. This was added to a solution of 6.74 grams of methyl dihydroxymalonate in 15 ccs. of water. Carbon dioxide was evolved when the two liquids were mixed, and a fine, white, crystalline precipitate formed in a few moments. The solution was chilled in ice water for five minutes and filtered, washed several times with cold water, then twice with methyl alcohol, and finally with cold ether. The product was pure white and finally granular. Six and three tenths grams were thus obtained from 6.74 grams of methyl mesoxalate. This product is quite pure, but can be recrystallized from methyl alcohol. Thus purified, it contracts slightly and melts at 154-155°, forming a clear liquid, which turns yellow and gives off a gas. Heated higher, the liquid forms a gum. On cooling, a yellowish crystalline body forms

in the upper part of the tube.

The analysis of the above product gave the following figures:

1. .3096 gr. gave 25.0 ccs. of Nitrogen at 746.2 mm. and 21.5°

2. .2201 " " 16.8 " " " " 748.8 " " 16.0°

1. .2419 " " .3288 gr. CO_2=.08966 gr. C, and .1033 g. H_2O=.01148 g H

2. .1876 " " .2554 " " =.06947 " " .0323 " " =.00915 "

Calculated for:-

	1.	2.
N = 8.64%	N = 9.02%	8.92%
C =37.03%	C = 37.07%	37.12%
H = 4.93%	H = 4.75%	4.87%

The formula given above is that of Methyl Hydrazotartronate. This substance is soluble in hot water, warm dilute sulphuric acid, hot 25% acetic acid, hot dilute hydrochloric acid, hot sodium carbonate solution, and cold alkalies. It is fairly soluble in hot methyl alcohol, acetone, acetic ether, and 95% alcohol. It dissolves with difficulty in cold methyl alcohol, benzene, carbon bisulphide, acetic ether, 95% alcohol, and in water. It is insoluble in ether and acetone.

When a portion of this crystalline body is heated in a

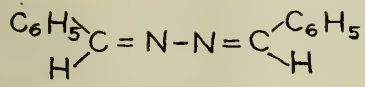
test tube, it melts, gives off a gas and a fragrant, greenish oil distills which crystallizes on cooling. Heated with silver nitrate there is no apparent reaction, but upon the addition of ammonium hydroxyde, a silver mirror is deposited, showing a strong reducing action. This reaction takes place slowly in cold solutions. Mercuric oxide is not reduced at once, but on long standing there is a slow reduction to metallic mercury. Thoroughly dried, and treated with phosphorus pentachloride, voluminous fumes of hydrochloric acid are given off. This proves the presence of hydroxyl groups. Hot concentrated hydrochloric and glacial acetic acids dissolve it, and on cooling, white crystals separate out. Allowed to stand in a thin layer in a dessicator over sulphuric acid.for several weeks, the product slowly changes to a colorless oil at the edges. Phosphorus pentoxide on the white body, forms very slowly a yellow crystalline product.

ACTION OF BENZALDEHYDE ON METHYL HYDRAZOTARTRONATE:- When 7.08 grams of this methyl hydrazotartronate are treated with two molecules of benzaldehyde in 45 ccs. of methyl alcohol, a

good yield is obtained of a fine yellow body, crystallizing in needle form. This has a melting point of 93°. when recrystallized from methyl alcohol. The analysis follows:-

.2122 g. gave 25.8 ccs. of nitrogen at 27° and 746.2 mm.

.2437 " " .2701 g. CO_2 = .1963 g. C and .1281 g. H_2O = .01423g.H.

Calculated for: 

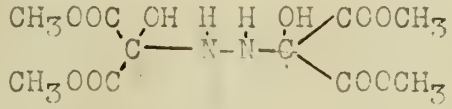
	1.	2.
C = 80.77%		C = 80.58%
H = 5.77%		H = 5.83%
N = 13.46%		N = 13.64
100.00%		100.05%

This compound is very soluble in ether, easily soluble in benzol, acetone, chloroform, carbon tetrachloride, hot methyl and ethyl alcohols, and hot ligroin. It is insoluble in water, and dissolves with difficulty in cold ligroin. Heated in a test tube, this substance gives off a colorless gas, and distill around 300°. These tests and the analysis show this product to be benzalazin, described by Curtius[1]. The mother liquor from the benzalazin crystals, when treated with phenylhydrazine gave a fine yellow precipitate which gave the correct melting point 163°, for the phenyl-hydrazone of mesoxalic acid. The water extract of the mother liq-

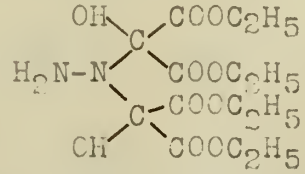
1) Jour. für Pr. Chemie. Vol. 39, p. 44.

our of the benzalazine, on standing in a desiccator for two weeks, contained crystals of the methyl dihydroxymalonate. These melted at 78° and when treated with hydrazine carbonate solution gave the original body, of 155° melting point, from which the benzalazine was formed, thus proving its identity as methyl dihydroxymalonate. Benzoic acid was also present in small quantities, and a fluorescent oil with an odor of benzaldehyde, this however was not studied.

From the above tests and reactions, it is probable that the structure of the white "155° body" corresponds to the following formula:



This provisional formula is further substantiated by a comparison of the reactions of this substance with those of the product of the corresponding reaction of hydrazine upon ethyl dihydroxymalonate, to which the following formula has been given provisionally[1]:



In this work upon methyl mesoxalate, it has been noticed that if methyl oxomalonate is mixed with one molecule of absolute alcohol, the temperature suddenly rises about 30°, its green color rapidly disappears, and upon cooling in ice water, large square

1) See Thesis of A. R. Koch, Page 15, This Laboratory- June 1907

crystals form. These have a melting point of 59-60°, and are fairly soluble in ether. This product was not studied further, owing to lack of time to carry out analyses and tests.

A STUDY OF THE PRODUCTS OF THE MOTHER LIQUOR FROM THE MESOXALIC ESTER CRYSTALS:- The mother liquor from the crystals of methyl dihydroxymalonate is a thick green oil of acid properties. It was worked up as follows:-

24.0 grams of the mother liquor dissolved in 30 ccs. of ether, were placed in a separatory funnel and carefully washed with about 40 ccs. of water. The yellowish green water solution which was separated, contained mesoxalic acid, with small amounts of oxalic acid, which later separated in crystalline form. The ether solution was dried with calcium chloride, and evaporated in a vacuum desiccator over sulphuric acid. This treatment yielded 12.0 grams of a nearly colorless oil (A), with a pungent irritating odor. Alcoholic potash on this oil gave a good yield of a yellow potassium salt, which, when recrystallized from alcohol, and treated with an acid, served as a means of obtaining a pure substance from the crude mixture of oils in the mother liquors.

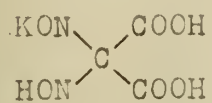
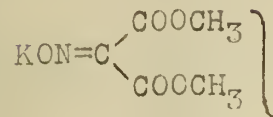
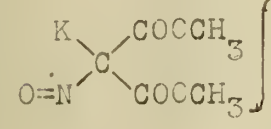
PREPARATION OF THE POTASSIUM SALT:- 20.0 ccs. of an absolute alcoholic potash solution containing 5.6 grams of potassium hydrate (1 molecule) were added to 16.1 grams of washed oil (A) in a small flask, and the temperature carefully kept below 0°. The potash solution was added slowly through a separatory funnel, to avoid heating, and a resulting gaseous decomposition. The canary yellow salt quickly began to separate out. Excess of alkali or heating causes a white salt to form, apparently due to saponification of an ester. When about 1/3 of the alkali was in, the mass became semi-solid and about 10 ccs. of absolute alcohol were added to facilitate stirring. When all the alkali was in, the flask was allowed to stand at 0° for five minutes, when it was quickly filtered and washed well with absolute alcohol, and finally with dry ether. The yield was 50% on the oil used. This potassium salt was purified by recrystallization from 90% alcohol, fromwhich it comes out in beautiful, canary-yellow leaflets with a silky lustre. Analysis of this salt for potassium gave the following figures:-

I) .2425 gr. of salt gave .1052 gr. of K_2SO_4

II) .2514 gr. of salt gave .1089 gr. of K_2SO_4

Calculated for:-

Found:-

			I	II
1.		K = 19.31%	19.44%	19.41%
2.		K = 19.59%		
3.				

This potassium salt does not melt, but if placed in a bath at 210° and the temperature quickly advanced, it turns red at 220-225° and decomposes around 230° giving off a gas, and finally becoming black. When a portion of the salt is placed in a test tube and heated over a flame, it explodes with a flash of purple flame, giving off white vapors, and a yellow oil is condensed in the hotter portions of the tube; a darkened residue is left at the bottom of the tube, which continues to give incipient explosions on further heating. This behavior is similar to that of the corresponding potassium salt of the ethyl ester already prepared.[1] The salt is slowly affected by light, turning a darker yellow. It is fairly soluble in water, and in 90% alcohol, slightly sol-

1) Am. Chem. Journal. Vol. 35, P. 484.

uble in acetone, and insoluble in ether, benzene, ligroin, carbon tetrachloride, and in chloroform. It is soluble in concentrated sulphuric, hydrochloric, and glacial acetic acids without color. Such a solution, when largely diluted, becomes yellowish green. Silver nitrate with an aqueous solution of the salt, forms, on evaporation, a yellow silver salt crystallizing in rosettes of needles. These soon darken in the light, and in a few days are entirely replaced by isomorphous metallic silver.

REGENERATION OF THE ACID FROM THE POTASSIUM SALT:- 15 grams of the pure potassium salt suspended in 75 ccs. of ether were placed in a separatory funnel. 75 ccs. of dilute sulphuric acid (1 1/4 molecules) were slowly added, the mass was vigorously shaken, and kept cool. The salt slowly dissolved. The ether solution was then carefully washed eight times with 25 ccs. of water, the last aqueous wash being strongly acid. It is noticible that the ether solution, while itself nearly colorless, gives to the wash water an intense yellow color. The ether was dried over calcium chloride, placed in a wide dish and evaporated in a vacuum desiccator over sulphuric acid. 11.1 grams of a nearly

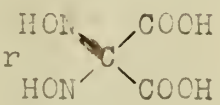
colorless oil (B) were thus obtained. When this is thoroughly dried for forty eight hours, it has but a pale yellow tinge. When the desiccator was opened, an odor, faintly suggestive of acetic acid and of red oxides of nitrogen, was noted. The oil in the dish, however, had a peculiar sweetish smell, faintly suggestive of green willow bark. This oil when analyzed, gave the following figures:-

1. .3136 grams gave 47.8 ccs. of Nitrogen at 24.5° and 738 mm.

2. .2444 " " 37.4 " " " " 24.0° " 735.65 mm.

1. .2721 g. gave .2156 g. CO_2 & .0724 g. H_2O =.0588 g. C & .00805 g. H.

2. .2551 " " .2000 " " " .0702 " " =.05454 " " .00780 " ".

Calculated for  Found:-

	1.	2.
C = 21.95%	C = 21.61%	21.38%
H = 2.44%	H = 2.95	3.05%
N = 17.07%	N = 17.06	17.10%

These results correspond accurately with the empirical formula, $C_3H_5N_2O_6$. The above structure appears probable for the constitution of this substance, though further study is necessary, and is in progress, to definitely settle this point.

Various tests were made on this oil. Its density is slightly greater than that of water, in which it is insoluble, although

one drop of the oil will color several litres of water yellow. It is easily soluble however, in alcohol, ether, acetone, chloroform, and carbon tetrachloride, giving colorless solutions. It is insoluble in ligroin. Upon treating this oil with alcoholic potash solution below 0°, a yellow potassium salt is obtained, decomposing about 230° when quickly heated, and is apparently identical with that from which the oil was made. Ammonium hydroxide gives a fine yellow crystalline product. Silver nitrate solution on the oil gives a brilliant yellow solution, but no other change. Ammonium hydroxide carefull added to this gives a yellow precipitate, which dissolves on warming, turning the solution red, but apparently gives no reduction. This oil while itself almost colorless, has a very powerful dyeing effect on silk and wool, the skin as well being at once colored a permanent yellow, precisely as is the case with nitric acid. A bit of the oil in a test tube of water, while itself practically insoluble gives, as stated, a bright yellowish green color to the water; if now concentrated sulphuric acid be added, the color entirely disappears. On dilution with water again, the color reappears. A similar effect is produced

with concentrated hydrochloric and glacial acetic acids. Apparently, water has a hydrating effect on the oil, forming an addition product, which gives colored ions. The action of concentrated acids in discharging the color appears to be due to an increased number of hydrogen ions. Under certain exact conditions, a 1.6% solution of hydrazine hydrate, used in slight excess on the oil, gave a clear yellow solution, which in 24 hours left a solid mass of fine crystals which appeared to be well defined hexagonal plates. This salt exploded like the potassium salt when heated in a test tube. The oil has a very pleasant, sweet taste, and is probably poisonous. On heating it in a test tube to 100-120°, distillation commences: from 120-130° decomposition sets in, red oxides of nitrogen are suddenly evolved, and a colorless liquid distills, the decomposition slowly continuing. The residual oil is insoluble in water, but has little coloring effect either on water or on the skin.

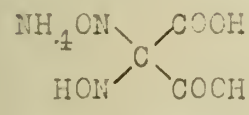
PREPARATION OF THE AMMONIUM SALT:- Concentrated ammonium hydroxide on the oil gives a yellow solution, which when carefully evaporated, leaves fine yellow crystals. The solution of

the oil in ether treated with dry ammonia gas, gives a fine pale yellow salt, which rapidly precipitates out in the ether, and seems quite pure. This ammonium salt was recrystallized from 95% alcohol, from which it came out, of a pure greenish yellow color.

Analysis:-

1. .2328 g. gave 48.5 ccs. of N at 752.75 mm. and 26° = .05509 g.N.
2. .2622 " " 54.6 " " " " 751.70 " " 26° = .06193
1. .2570 " ".1802 g. CO_2 & .1018 g. H_2O =.049145 g. C & .01131 g.H.
2. .3045 " ".2112 " " " .1138 " " =.057600 " " " .012644 "

Calculated for:-



	Found:- 1.	2.
C = 19.88%	C = 19.12%	18.91%
H = 3.85%	H = 4.40%	4.15%
N = 23.20%	N = 23.66%	23.62%

The salt is very soluble in water and hot alcohol. It is fairly soluble in acetone, and in cold alcohol. It dissolves with difficulty in acetic ether, and is insoluble in ether, benzene, and in ligroin. The salt can be boiled in water, or alcohol, without apparent decomposition, the hot solution is red, but upon cooling, the solution becomes a light yellowish green. When placed in a bath at 175°, and heated quickly, it decomposes at 187-188° and gives off a gas. On being heated to a rather high temperature

on a platinum spatula, it suddenly gives off a combustible gas. if very carefully heated in a test tube, it sublimes, apparently unchanged, at about 100-125°. If the temperature is allowed to rise slightly above this point, the mass reddens, and a sudden gaseous decomposition sets in and rapidly passes throughout the mass. This fact renders the analysis of the salt difficult, and explains the discrepancy in the above figures.

THE ACTION OF HYDROXYLAMINE ON METHYL DIHYDROXYMALONATE:-

V. Meyer[1] made isonitrosomalonic acid, by treating mesoxalic acid with hydroxylamine. Methyl isonitrosomalonate, as made by Bouveault and Wahl[2], crystallizes in long white needles melting at 66-67°. In order to study methyl isonitrosomalonate, an attempt was made to prepare it in the following manner:-

10 grams of methyl dihydroxymalonate were treated with a solution of 4.76 grams of hydroxylaminehydrochloride and 3.66 grams of sodium carbonate dissolved in 9 ccs. of water. When the crystals methyl dihydroxymalonate were dropped into the hydroxylamine solution, the temperature rose 10°, and a slight yellow color was

1) Ber. d. Deut. Chem. Ges. Vol. 16, Page 1621.
2) Bull. Soc. Ch. de Paris. Vol. 29, Page 961.

duce a hot ammoniacal solution of silver nitrate. A prussic acid smell is noted when it is boiled with water, as is mentioned by Victor Meyer[1], and Baeyer[2]. in the case of isonitrosomalonic acid. under the same conditions. Owing to lack of time, an analysis has not been made on this substance.

From the melting point, crystal form, action of hot water, and the solubilities, this body is in all probability the oxime of methyl oxomalonate. This being the case, and from the simple fact that it is miscible with water and does not color the aqueous solution in the least, it is apparent that the pale yellow oil B (Page 20) from the potassium salt above described, cannot be an isonitrosomalonic ester. The substances herein described are being further studied in this laboratory.

The main conclusions drawn from this work are as follows:-

1. The method here described gives a larger yield (78%) of methyl mesoxalate than any hitherto described, and has the advantage of being rapid and inexpensive.

1) Ber. d. Deut. Chem. Ges. Vol. 16, Page 1621.
2) Ann. Chem. (Liebig's.) Vol. 209, P. 211.

2. The by-products of this reaction are unstable, decomposing at ordinary temperatures with the evolution of gases, and formation of acetic, mesoxalic, and oxalic acids and esters, and also unstable esters containing nitrogen which have somewhat remarkable properties, and are of peculiar scientific interest.

3. Hydrazine hydrate, or carbonate, produces on methyl mesoxalate a crystalline product called methyl hydrazotartronate. The use of hydrazine carbonate gives a product of much higher yield and purity than hydrazine hydrate. This substance is of slightly greater stability than the product of the corresponding reaction of hydrazine solutions on ethyl mesoxalate.

Laboratory of Organic Chemistry,

May 31, 1907.

- Finis -

P. T. Tarwoski.

This work was done in conjunction with Prof. R. S. Curtiss.

UNIVERSITY OF ILLINOIS-URBANA
3 0112 079824857